Auger decay of the C $1s^{-1}2\pi^*$ resonance in carbon monoxide: vibrationally and angularly resolved spectra

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INTRODUCTION

Resonant photoexcitation of carbon 1s electrons to the lowest empty molecular orbital, $2\pi^*$, gives rise to the dominant pre-edge feature in the C 1s photoabsorption spectrum. The C $1s\rightarrow2\pi^*$ excitation displays a vibrational progression corresponding to the population of different levels of the excited state, in which the strongest $\nu=0$ peak is accompanied by transitions to the higher levels, $\nu=1$ and 2, with rapidly decreasing intensity. In previous experiments [1,2], it has been possible to completely resolve the vibrational structure of the Auger decay spectra of the lowest level of the $1s^{-1}2\pi^*$ state, whereas the decay spectra of the higher levels have been obtained only with considerably lower experimental resolution. Vibrationally resolved Auger electron spectra from the higher vibrational levels provide richer and more precise information about the shapes of the potential energy curves and transition intensities to different final ionic states. The present experiment provides such information, which is compared with the latest theoretical results. In addition, angular distributions of the individual vibrationally resolved peaks in the Auger electron spectra have been obtained.

To obtain a more complete picture of the Auger decay processes in reonantly excited CO, we employed two complementary experimental techniques -- high-resolution angle-resolved measurements at the resonance maxima using hemispherical electron energy analyzer and electron time-of-flight (TOF) measurements in combination with two-dimensional mapping of the photon and electron kinetic energy.

EXPERIMENT

The experiment was carried out at the undulator beamline 9.0.1 at the ALS (later relocated to 10.0.1). VUV radiation was monochromatized with a spherical grating monochromator using a grating with a groove density of 2100 lines/mm. For the high-resolution measurements, an end station based on the Scienta SES-200 hemispherical electron anayzer and designed for angle-resolved gas-phase studies was used. The analyzer is rotatable in a plane perpendicular to the propagation direction of the beam of linearly polarized photons, allowing studies of electron angular distribution. An electron energy resolution of 25-30 meV (at 40 eV pass energy) was used for these measurements. A photon bandwidth of about 60 meV was used when recording the Auger electron spectra and a smaller bandwidth of 45 meV was used for additional lineshape studies.

The data set for two-dimentsional imaging was collected using two electron time-of-flight analyzers, mounted 125.3° apart and perpendicular to the photon beam [3]. The photon energy was scanned over the resonance in 20 meV steps using 60 meV bandwidth.

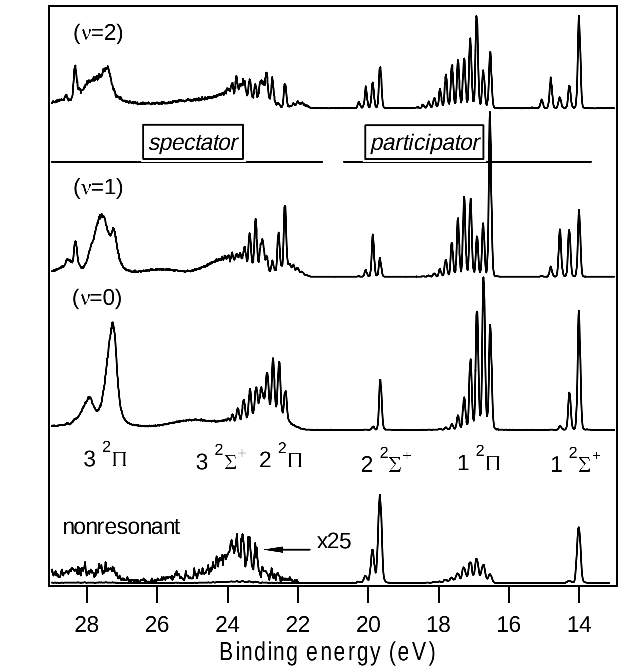

Figure 1. Electron energy spectra of the decay from the C $1s^{-1}2\pi^*$ ν=0,1,2 resonances, taken at the magic angle relative to the polarization plane. Also shown is a nonresonant photoelectron spectrum measured at hν=280 eV.

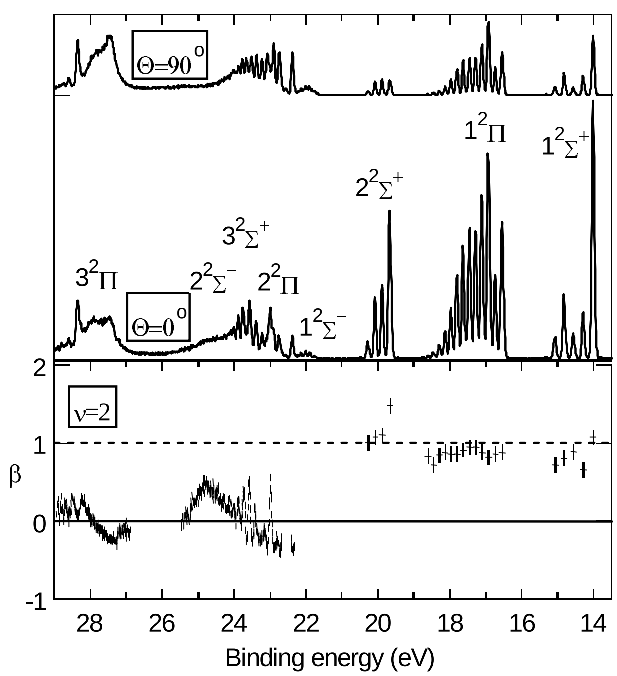

Figure 2. Electron energy spectra of the decay from the ν=2 level of the C $1s^{-1}2\pi^*$ resonance, taken at 0° and 90° relative to the polarization plane. Lower panel shows the anisotropy parameter β.

RESULTS

Auger electron spectra were measured at selected photon energies, corresponding to the C 1s→2π* absorption maxima, using the hemispherical analyzer. The spectra are shown in Fig. 1, together with a photoelectron spectrum taken well below the resonant absorption energy. The spectra were measured at 54.7° relative to the polarization plane of the light and are scaled to equal intensity for the ease of comparison. The overall intensity of the spectra taken at the ν=1 and 2 absorption peaks is about 13% and 1.4%, respectively, of the intensity of the spectrum taken at the strongest ν=0 peak.

The vibrational envelopes of the spectra in Fig. 1 can be compared with theoretical simulations [4]. There is excellent agreement between theory and experiment, indicating that the calculated potential energy curves describe the core-excited and final ionic states very well.

Fig. 2 shows angle-resolved Auger electron spectra from the weakest n=2 level of the resonance. The anisotropy parameter β varies significanty within the vibrational envelopes of the low-binding energy states. These CO^+ states are also accessible by direct photoionization and we therefore ascribe the variations in β to the contribution from and interference with the nonresonant photoionization process. The states at higher binding energies are not accessible by direct photoionization and the spectator Auger decay to these states provides the only opportunity for electron spectroscopic studies. There are a number of strongly overlapping ionic states present in this energy region, with bonding and antibonding character. The present high-resolution spectra allow us to indentify the character of these states and develop the theoretical model correspondingly.

The comparison of the Auger decay spectra from different levels of the excited state allows better assignment of these states. It can be seen from Fig. 2 that the β parameter displays strongly oscillating behavior in the high binding energy region. From these oscillations, we were able to determine the angular properties for the Auger transitions to individual electronic states.

TWO-DIMENSIONAL IMAGING

An intensity map of electron emission following photoexcitation of CO across the C 1s$\rightarrow$2π* resonance is shown in Fig. 3. The map is constructed from a series of electron energy spectra recorded at small steps over a broad range of photon energies. The X and Y axes of the map represent the binding energy of emitted electrons and the energy of absorbed photons, respectively.

2D images provide a direct means to observe lifetime vibrational interference effects by following the intensities of individual vibrational peaks in the Auger electron spectra as a function of photon energy. The intensity of the ν'=1 line of the 1 $^2\Sigma^+$ transition reaches its second maximum (corresponding to the ν=1 absorption peak) at lower photon energy than does the intensity of the neighboring ν'=0 and 2 lines. Also, the minumum between the first and second maxima is very shallow compared to the minima in the intensity of the ν'=0 and 2 lines. Similar behaviour can be seen in the vibrational envelopes of the 1 $^2\Pi$ and 2 $^2\Sigma^+$ final states. These effects are clear indications of significant vibrational lifetime interference between different Auger decay pathways, which naturally emerges in the single-step treatment of the excitation-deexcitation processes.

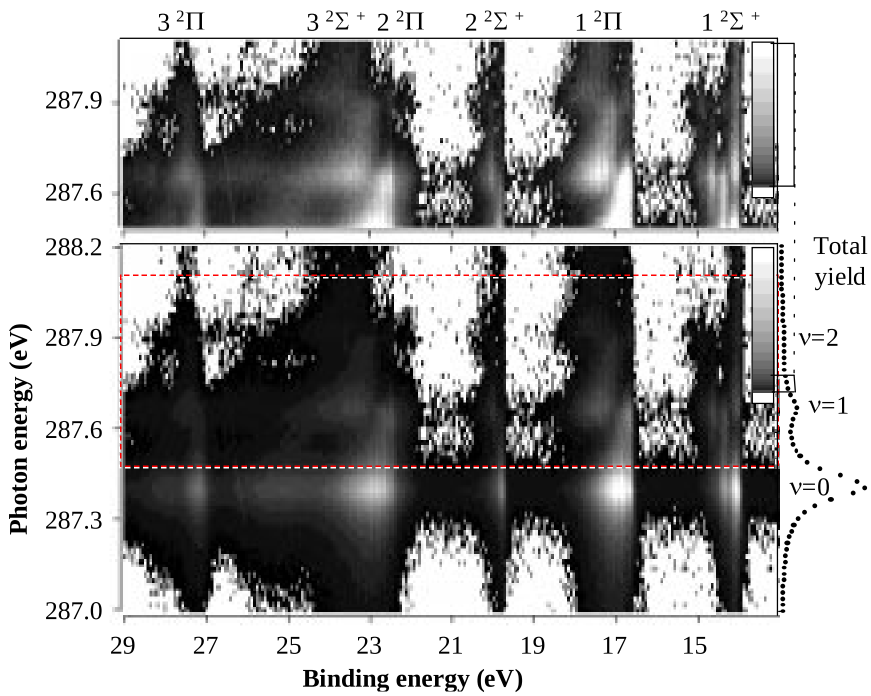

Figure 3. Intensity map of electron emission over the C 1s$\rightarrow$2π* photoexcitation region as a function of electron (X axis) and photon (Y axis) energies. The area between dashed lines is reproduced above the main panel, emphasizing low-intensity areas. The right-hand panel shows the integrated electron yield over the given energy range. Assignment of final states is given above the map.

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